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## GLASS QUALITY AND ADHESION EVALUATION IN GLASS FIBER PRODUCTION

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The processes occurring during the production of glass fiber from glass with different chemical composition and the influence of hydrostatic forces, surface tension, and internal friction on the formation process are examined. The critical fiber formation temperature under conditions where the viscosity and surface tension of the molten glass are of different magnitude is determined. A new approach to evaluating the capability of glass to form glass fiber according to the ratio of the surface tension to the viscosity is proposed. A computational method of evaluating the formation rate of glass fiber with different diameters is given for the example of E glass. Some mechanisms of adhesion of organic polymers and protein molecules to a glass surface are presented.

**Key words:** glass fiber, process parameters of formation, viscosity, surface tension, adhesion interactions.

The rapid advancement of modern technology is making it necessary to create new, artificial materials with technical, technological, and performance properties which are superior to those of natural materials. Since the chemical and mineral composition, structure, and fabrication conditions can all be varied, the physical–mechanical, chemical–biological, optical, electrical, and other properties of the new technical materials can be varied over quite wide ranges. Glass fiber and different types of composite materials based on glass fiber have a special place among these materials.

Glass-fiber materials are characterized by substantial thermal and chemical stability, high mechanical strength with relatively low density, good electric, heat, and sound insulation properties as well as inflammability. The glass compositions of glass used for the production of glass fiber (GF) and the assortment of articles using glass fiber is continually expanding; GF-based articles are finding applications in electrical engineering, aviation, aerospace, defense, medical, and other areas of technology.

Together with the glasses which are conventionally used to manufacture GF, new types of glass are actively being developed and adopted: high-modulus glass with low and zero alkali concentration, whose rheological properties and quality differ considerably from those of glass with known compositions.

The formation and, specifically, fiber formation capability of glass is determined by the ratio of two temperature-dependent process parameters — internal friction (viscosity), which is expressed by the dynamical coefficient of viscosity  $\eta$ , and the surface tension  $\sigma$ . The ratio of the internal friction  $P_\eta$  and surface tension  $P_\sigma$  forces determines the flowability of molten glass in the high-flow state within the formation temperature intervals.

Conventionally, the capability of glass to form fiber is characterized by the ratio of the viscosity to the surface tension of the melt [1–3]. This ratio is the fiber-formation indicator. Since the surface tension of quartz and silicate melts,

TABLE 1.

| Glass            | Content, wt. %   |                               |                                |      |      |                   |
|------------------|------------------|-------------------------------|--------------------------------|------|------|-------------------|
|                  | SiO <sub>2</sub> | B <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO  | MgO  | Na <sub>2</sub> O |
| E composition    | 54.0             | 10.0                          | 14.5                           | 16.5 | 4.0  | 1.0               |
| No. 11           | 76.5             | —                             | 3.5                            | —    | —    | 20.0              |
| No. 28           | 56.0             | —                             | 5.0                            | 22.0 | 6.0  | 11.0              |
| VMP              | 58.5             | —                             | 26.1                           | —    | 15.0 | 0.4               |
| VM-1             | 58.9             | —                             | 24.0                           | —    | 15.2 | 1.9               |
| Alkali-free      | 64.3             | —                             | 13.5                           | 16.1 | 4.3  | 1.8               |
| Composition Ts4* | 61.0             | 4.5                           | 7.0                            | —    | 10.0 | 15.5              |
| Quartz [4]       | 99.95            | —                             | 0.05                           | —    | —    | —                 |

\* In addition, Ts4 glass contains 2.0% TiO<sub>2</sub>.

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TABLE 2.

| Material     | Measurement temperature, °C | Viscosity, Pa · sec | Surface tension, N/m | Fiber-formation indicator |                       | GF formation rate, m/sec |
|--------------|-----------------------------|---------------------|----------------------|---------------------------|-----------------------|--------------------------|
|              |                             |                     |                      | $\eta/\sigma$ , sec/m     | $\sigma/\eta$ , m/sec |                          |
| Glycerin     | 20                          | 10                  | 0.065                | 1.54                      | 0.00650               | 650                      |
| Oil          | 20                          | 10                  | 0.033                | 3.03                      | 0.00330               | 330                      |
| E glass 1400 | 1400                        | 100                 | 0.300                | 333.00                    | 0.00300               | 300                      |
|              | 1300                        | 250                 | 0.301                | 831.00                    | 0.00120               | 120                      |
|              | 1200                        | 600                 | 0.302                | 1990.00                   | 0.00050               | 50                       |
|              | 1100                        | 2000                | 0.305                | 6560.00                   | 0.00015               | 15                       |
|              | 1000                        | 8000                | 0.308                | 26000.00                  | 0.00004               | 4                        |
| Quartz glass | 2200                        | 10,000              | 0.500                | 20000.00                  | 0.00005               | 5                        |
| VMP          | 1500                        | 5                   | 0.520                | 9.62                      | 0.10400               | 10,400                   |
| VM-1         | 1500                        | 10                  | 0.510                | 19.60                     | 0.05100               | 5100                     |
| Glass:       |                             |                     |                      |                           |                       |                          |
| No. 28       | 1380                        | 5                   | 0.480                | 10.42                     | 0.09800               | 9800                     |
| Ts4          | 1250 – 1300                 | 350                 | 0.450                | 778.00                    | 0.00130               | 130                      |

in contrast to the viscosity, in the temperature range of fiber formation varies very little, glass melts for obtaining different types of fibers are classified as high-viscosity melts for  $\eta/\sigma > 1000$  and low-viscosity melts for  $\eta/\sigma < 100$ .

The dimensions (sec/min) of the fiber-formation indicator reflect the dependence of the time on the path traversed, i.e., the time for the molten glass mass to traverse a distance of 1 m. It is more logical to express this indicator by the inverse ratio of the surface tension to the internal friction, i.e.,  $\sigma/\eta$ ; then, the corresponding dimensions are m/sec. Thus, the fiber-formation indicator of glass reflects the dependence of the velocity of molten glass under surface tension on the internal friction. The chemical compositions of the glasses are presented in Table 1, and the computational results for the rates of fiber formation from E glass, quartz glass, and high-modulus glass as a function of  $\eta/\sigma$  and  $\sigma/\eta$  are presented in Table 2.

The computational results obtained for the fiber-formation rate as a function of  $\sigma/\eta$  are close to reality. Fiber is produced by different methods from glass with the compositions presented and with different pulling velocities. Thus, the pulling velocity for 14  $\mu\text{m}$  in diameter E-glass fiber, pulled by a mechanical method on SPA-6S glass-strand equipment, lies in the range 50 – 70 m/sec. Fiber made with No. 28 glass is produced by a pneumatic method of vertical blowing with steam; the velocity of the energy carrier in this method reaches 500 – 600 m/sec. Ultra- and microthin Ts4-glass fibers are produced by the centrifugal-spinneret-blowing method of inflating the primary glass strands by a high-temperature gas flow, likewise at ultrasonic velocities. The computational data for the rate of formation of fiber from this glass are close to the E-glass fiber indicators at the stage when the primary fibers exit the spinneret of a centrifuge rotating at 2500 – 3500 rpm, which permits fiber formation at subsonic velocities [5].

For engineering calculations of fiber-formation processes it is more convenient to use not the duration of the formation process but rather its lineal velocity, determined by the ratio  $\sigma/\eta$ . The formation time of glass fiber is 0.2 – 1.0 sec depending on the volume of the spinneret “onion.” Over this period of time the flow velocity of the molten glass increases from the bottom edge of the spinneret to the top of its “onion,” where the thinning of the molten glass as it is stretched into a glass fiber stops, by a factor of  $10^5$  –  $10^6$ . Therefore, it can be assumed that the rate of formation of a fiber from glass with any particular composition can be determined according to the indicator  $\sigma/\eta$  taking account of the acceleration of the flow of the molten glass during production:

$$v = \sigma/\eta \times 10^5 \text{ (m/sec)}.$$

A problem arising in the production of textile GF is the sharpness of the cutoff of the fibers during production, which depends on the temperature of the glass-melting vessels and the spinnerets. As the temperature decreases, the sharpness of fiber cutoff increases with increasing viscosity of the molten glass. However, when temperature increases above definite values the sharpness of the fiber cutoff also increases, which is a consequence of a decrease of the viscosity of the molten glass. Here, molten glass in the form of streams or drops is observed to slip through a spinneret, i.e., a transition to free flow occurs. The diameter of the fiber produced likewise is observed to increase with increasing process temperature.

Since the internal friction and surface tension are the main process parameters for glass formation, the stability of the glass depends on the ratio of these two acting forces. In other words, the continuity of the structure and surface of the glass formed is preserved provided that the forces  $P_\eta$  and  $P_\sigma$  are comparable in magnitude. If one exceeds the other, the fi-

ber breaks, though by different mechanisms. Evidently, the glass production temperature at which these two forces are equal to one another is the critical temperature  $T_{cr}$ . If the fiber-formation temperature  $T_f > T_{cr}$ , fiber cutoff occurs by a viscous-flow deformation mechanism because the surface tension force is greater than the viscosity force. For  $T_f < T_{cr}$  the sharpness of fiber cutoff is of an elastic-brittle mechanical fracture character, which according to Hooke's law holds at temperatures below the Littleton softening temperature, which corresponds to glass viscosity  $10^{6.5}$  Pa · sec.

To evaluate the formation velocity of a glass fiber it is necessary to know the character of the relation between the internal friction forces acting in the molten glass, the surface tension, and the hydrostatic pressure:

$$P_h = \rho gh, \quad P_\sigma = 2\sigma/D, \quad \text{and} \quad P_\eta = \eta/\tau,$$

where  $P_h$  is the hydrostatic pressure in the glass mass, Pa;  $P_\sigma$  is the surface tension force, N;  $P_\eta$  is the internal friction force, N;  $\rho$  is the density of the molten glass, kg/m<sup>3</sup>;  $g$  is the acceleration of gravity, m/sec<sup>2</sup>;  $h$  is the height of the surface level of the molten glass, m;  $\sigma$  is the surface tension of the molten glass, which is taken to be constant and equal to 0.3 N/m (E glass);  $D$  is the diameter of the spinneret, m; and,  $\tau$  is the formation time, sec.

The molten glass flows out of the spinneret provided that  $P_h > P_\sigma$  and both forces are constant and work to overcome the viscosity forces  $P_\eta$ . Taking this into account, the glass formation time is determined separately: under the action of the surface tension —  $\tau_\sigma$  and gravity —  $\tau_g$  [6]:

$$\tau_\sigma = Kr \frac{\eta}{\sigma} \quad \text{and} \quad \tau_g = Ms \frac{\eta}{m},$$

where  $K$  and  $M$  are coefficients,  $r$  is the radius of curvature, m, and  $m$  is the mass of the glass formed, kg.

These relations, which include the ratio  $\eta/\sigma$  of the viscosity to the surface tension of the molten glass, can be used to calculate the formation time of small spherical articles with a small radius of curvature, such as glass fibers, capillaries, microspheres, and other articles with small mass and small dimensions.

The critical temperature and the corresponding critical viscosity were determined on the basis of the conditions that the internal friction forces and the surface tension forces are equal to each other in magnitude:

$$P_\sigma = P_\eta.$$

Then

$$\eta_{cr} = \frac{\sigma\tau}{r}.$$

For a 10  $\mu$ m in diameter fiber with composition E the computed critical viscosity is  $\eta_{cr} = 6 \times 10^2$  Pa · sec. When the viscosity decreases below this limit, the surface tension

forces become predominant and the GF formation process becomes unstable.

The computed critical viscosity of the E-glass melt, equal to  $6 \times 10^2$  Pa · sec, is close to reality. The experience gained in producing GFs shows that melt viscosity  $10^2$  Pa · sec is optimal for fiber formation. Consequently, when the properties of the finished glasses are evaluated their parameters are referred to the temperature corresponding to this viscosity  $T_{100}$ . The GF production interval characterized the temperature range where the melt viscosity varies from  $10^2$  Pa · sec to a value corresponding to the upper limit of crystallization  $T_{ulc}$ , i.e.,  $\Delta T = T_{100} - T_{ulc}$ . The final properties of the glasses are considered to be optimal when  $\Delta T$  is a positive number.

Analysis of glass-fiber formation processes showed that the method used to calculate the formation rates according the ratio  $\sigma/\eta$  is applicable to the production of micro and nano size glass articles in the range from sub- to supersonic production velocities. The temperature and time gradients of the viscosity of molten glass in the formation zone are determined by the spinneret parameters — diameter, height, thickness of the wall — and by the cooling system.

High-modulus glasses and ultra- and microthin fibers based on them are of special interest not only for technology but also for medicine. Glass fibers with high SiO<sub>2</sub> content find applications in implantology for fabricating dental prostheses and in-bone implants. This is because silicate glasses are hydrophilic and easily hydrated with numerous polar  $\equiv$ SiOH groups and MeOH groupings (Me — Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>) with different charge being formed. Experience in using silicophosphate implants in clinical practice has shown that the presence of OH groups in them gives good biological compatibility with the physiological medium in the human body, while the  $\equiv$ SiOH groups stimulate histogenesis of hard (bone) and soft (connective, cartilaginous) tissues [7]. The change in the hard-elastic properties of glass-fiber composite materials and the diameter and orientation of the filler fibers in the matrix makes it possible to cultivate selectively on the surface of an implant one or several types of cell lines that react to specific biomechanical stimuli. It has been established that osteogenic cells attach to and grow on only fibers with diameter greater than 9  $\mu$ m, while fibrous and connective tissue cells will grow on fibers of any size. Highly elastic organosilicon silicone implants permit binding with cartilaginous cells, which makes it possible to use such implants as prostheses for finger joints while the hard composite materials based on silicate glasses serve to reconstruct defects of the bone tissue.

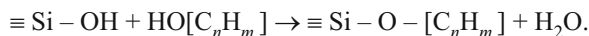
Dental root implants fabricated from high-modulus quartz fiber oriented along the implant height, whose chemical stability and mechanical strength match those of dental tissues, have appeared on the world market for medical materials. On the basis of texture and structure such prostheses are glass-fiber composite materials, whose individual oriented layers are fractions of a micron thick. High-modulus

silicon-containing fibrous materials with properties at this level can be developed once high-precision controllable processes for the formation of glass fibers and further development of the scientific principles of formation in application to concrete properties of glasses are developed.

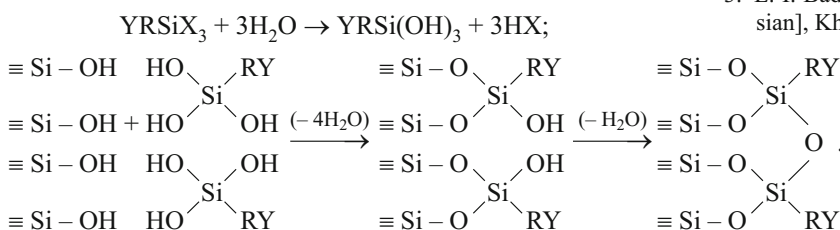
It is impossible to design GF-based high-technology composite materials without understanding the adhesive interactions which occur on the surface of a fiber.

The presence of different cations in the structure of glass affects not only the strength of the bonds  $\equiv \text{Si} - \text{O} -$  and  $= \text{Al} - \text{O} -$ , determining the strength and physical-chemical characteristics, but also the properties of the surface layers of the glass which participate in the formation of the glass-fiber – finishing-coat or glass – collagen bonds in the physiological medium. In both cases the adhesion interactions are determined by chemical reactions of the surface layers of the glass with the functional groups of the organic molecules, the electrostatic interactions between protein or finishing-agent molecules and the surface of the material, and the mechanical flow of the adhesive (finishing agent) into the pores and cracks of the substrate surface.

In the first place, strong bonding of the finishing-agent or protein molecule on a glass surface is obtained by dehydroxylation or deprotonation reactions of numerous  $\equiv \text{Si} - \text{OH}$  groups with the formation of  $\equiv \text{Si} - \text{O} - \text{C} \equiv$  and  $\equiv \text{Si} - \text{C} \equiv$  bonds. For example, protein attachment in the physiological medium in the body occurs according to the following reaction:



The attachment of a silane finishing-agent to the surface of a GF occurs similarly:



The groups  $= \text{Al} - \text{OH}$ ,  $= \text{Ca} - \text{OH}$ , and  $= \text{Mg} - \text{OH}$  can also participate in polycondensation reactions.

Silicon, like carbon, contains four electrons in the outer *sp* orbital, but unlike carbon its electronic *d* orbital, which is

capable of participating in the formation of a donor-acceptor bond, for example, with an amino group, forming a  $\equiv \text{Si} - \text{N} =$  bond, is unoccupied.

Van der Waals interactions (interaction between permanent or between permanent and induced dipoles), ion – dipole interactions, and hydrogen bond formation are all possible in multicomponent silicate glasses containing molecules and alkali-earth oxides.

Electrostatic bonds between protein or finishing-agent molecules and the surface of the material can also appear. The strength of these bonds is negligible compared to valence bonds, but the strength of the bonding of organic molecules to a glass surface is adequate because the number of bonds is so large.

Analysis of the fiber formation from glass with different chemical compositions has shown that the following process parameters should be taken into account when developing formation regimes using different production methods:

the viscosity of the glass mass at the critical temperature  $T_{\text{cr}}$ , when the internal friction forces are equal in magnitude to the surface tension forces;

the formation temperature  $T_f$  with respect to the upper limiting temperature of crystallization  $T_{\text{ulc}}$  and  $T_{\text{cr}}$ , i.e.,  $T_{\text{ulc}} < T_f < T_{\text{cr}}$ ;

the range of production velocities in for fibers with different diameters; and, the fiber formation time.

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